

KOLOKOLOV, V.K.; MOLGINA, G.M.

Protecting coatings of bridges. Put' 1 put. khoz. 9 no.7:
15-16 '65.

(MIRA 18:10)

1. Rukovoditel' gruppy Mostoispytatel'noy laboratorii Moskovskogo instituta inzhenerov zheleznodorozhnogo transporta (for Kolokolov).
2. Starshiy inzh. laboratorii zashchitnykh pokrytiy Vsesoyuznogo nauchno-issledovatel'skogo instituta zheleznodorozhnogo transporta Ministerstva putey soobshcheniya (for Molgina).

MOLHO

SORIN, E., Dr.; BELIGAN, Gr., dr.; STEFANESCU, Carmen, dr.;
MOLHO, M., dr.

Non-hemorrhagic complications of heparin therapy. Med.
int., Bucur. 3 no.7:1064-1066 Nov 56.

1. Lucrare efectuată în Clinica medicală Spitalul "Brincovenesc"
director: prof. R. Brauner.

(HEPARIN, inj. eff.

non-hemorrh. disord. caused by heparin ther.)

(FEVER, etiol. & pathogen.

heparin ther. causing chills & fever)

(SKIN DISEASES

rash, urticaria, pruritus & other disord. caused by
heparin admin.)

(ALLERGY, etiology & pathogenesis
heparin)

BRAUNER, R., Prof.; MOLHO, M., dr.; SCHONFELD, L., dr.;
CIGULESCU-AUDIZZIO, M., dr.; PANDELESCU, L., dr.

Notes on a case of erythroblastic anemia. Med. int., Bucur.
8 no.2:211-219 Apr-May 56.

1. Clinica medicala a Spitalului Brincovenesc.
(ANEMIA, ERYTHROBLASTIC
diag., clin. & hematol. aspects)

BERCEA, O., Dr.; MOLHO, M., dr.

Respiration function tests in clinical study of internal diseases. Med.int.,Bucur. 8 no.5:631-649 Sept 56.

1. Lucrare efectuata in Clinica fiziologica I.M.F. Clinica medicala I.M.F. din Spitalu Brincovenesc.

(RESPIRATION, function tests

in internal dis., methods & diag. value)

(MEDICINE, INTERNAL

diag. value of resp. funct. tests in internal dis.)

MOLHO, M.; SCHONFELD, L.

Respiratory acidosis. Med. int., Bucur. 9 no.8:1230-1245 Aug 57.

I. Lucrare efectuata in Clinica medicala a Spitalului "Brincovenesc"
Director: prof. R. Brauner.

(ACIDOSIS

resp., physiopathol. & ther.)

(RESPIRATION

resp. acidosis, physiopathol. & ther.)

1/1
BULGARIA

MOLHOVA, E., Central Laboratory of Genetics, Academy of Agricultural Science

"Hybridization Between *Capsicum Annuum* L. ($2n = 48$) and *Capsicum Pubescens* R. et P. ($2n = 24$)"

Sofia, Doklady Bolgarskoy Akademii Nauk, Vol 19, No 3, 1966, pp 225-228

Abstract: [English article] Since in scientific literature there are no data concerning the crossing of *Capsicum pubescens* R. et P. with other species of the *Capsicum* genus, the author reports on her experiments in this direction comprising more than a thousand crossings carried out over the 1962-65 period. The analysis of the results shows that 1) the use of higher-ploid parent in crossing represents a promising although difficult method of overcoming the incrossability between *Capsicum annuum* L. and *C. pubescens* R. et P. *C. annuum* ($4x$) participated as female parent and *C. pubescens* R. et P. ($2x$) as male parent; 2) the sesquidiploid in F_1 *Capsicum annuum* x *C. pubescens* ($3x$) possesses the traits of both parents, is of the intermediary type of heredity, and forms fruits which, however, are seedless, so that the hybrid is sterile; 3) the meiosis in PMC of the sesquidiploid *Capsicum annuum* x *Capsicum pubescens* ($3x$) proceeds with considerable disturbances, as a result of which microspores are formed with micronuclei from which nonviable pollen grains with differing ploidy are formed. There are 2 Bulgarian, 1 Soviet, and 4 Western references. Manuscript received, 14 Dec 65.)

1/1

SOV/112-58-2-2143

Translation from: Referativnyy zhurnal, Elektrotehnika, 1958, Nr 2, p 56 (USSR)

AUTHOR: Lyapich, A. V., and Molibashko, I. K.

TITLE: AC Operation of an Electromagnetic Relay
(Rabota elektromagnitnogo rele na peremennom toke)

PERIODICAL: Sb. stud. nauchn. rabot Belorussk. politekhn. in-t, 1957, Nr 3,
pp 126-128

ABSTRACT: The article presents the best results of the utilization of an EF-100 24-v electromagnetic relay in AC circuits with no time element and with a short-circuited turn applied, such relays can endure AC energizing of their winding for 10-12 minutes. The thermal durability of the winding is considerably higher than under DC (the DC 24-v relay can be supplied with 220-v AC). Relays with other winding data should be rewound. Operating time on AC is 0.01-0.02 seconds; i.e., it is less than with DC supply.

V.M.Kh.

Card 1/1

KESSEL', N.K.; OVCHINNIKOV, E.V.; KUCHUR, Ye.S.; GALKIN, P.A.; MOLIBOSHO,
V.A., red.

[Equipment and devices for assembling structural elements] Oboru-
dovanie i prispособleniia dlia montazha stroitel'nykh konstruktsii.
Minsk, Redaktsionno-izdatel'skii otdel BPI im. I.V.Stalina, 1960.
48 p.

(MIRA 14:6)

(Building—Tools and implements)

(Precast concrete construction)

ODEL'SKIY, E.Kh., prof., doktor tekhn. nauk, zasl. deyatel' nauki i tekhniki BSSR, red.; MOLYBOSHKO, V.A., red.; ~~MOLIBOSHKO, V.A., red.~~; NEKHAY, V.T., red.; DUBOVIK, A.P., tekhn. red.

[Proceedings of the Interuniversity Conference on Problems of Heating Residential and Public Buildings] Trudy Mezhvuzovskoi nauchnoi konferentsii po problemam otopeniia zhilykh i obshchestvennykh zdani, Minsk. 1962. Minsk, Izd-vo MVSS i PO BSSR, 1962. 285 p. (MIRA 15:11)

1. Mezhvuzovskaya nauchnaya konferentsiya po problemam otopeniya zhilykh i obshchestvennykh zdaniy, Minsk, 1962. (Heating--Congresses)

MOLIBOZHKO, A.P.; ROZENBERG, A.M.

Efficient method for the current maintenance of tracks. Put' i
put.khoz. 7 no.9:6-8 '63. (MIRA 16:10)

1. Nachal'nik sluzhby puti Donetskoy dorogi (for Molibozhko).
2. Nachal'nik tekhnicheskogo otdela sluzhby puti Donetskoy dorogi
(for Rozenberg).

MOLICKA-HANIAWETZ, A.

Poznaj sakład flotacyjny (Become acquainted with a flotation establishment), by A. Molicka-Haniawets. Reported in New Books, (Nowe Książki), No. 6, March 15, 1956

MOLICKA-HANIAWETZ, A.

7

Calamine ore flotation. J. Adamcaka and A. Molicka-Haniawetz. *Prace Inst. Hutniczych* 10, 269-75 (1958) (English and Russian summaries).--The ore from the mine Orzel Bialy consists mainly of smithsonite in a 10-40- μ grain, often covered with a thin (few μ) layer of limonite. The fine grain of smithsonite, and its dispersion, necessitate a thorough milling, which results in high losses of Zn. As flotation agents HCl and AcOH solns. of primary aliphatic amines, particularly hexadecylamine, were most effective (used in amt. of about 0.8 kg./ton). This process is not feasible economically. L. G. Manitius

JL

Y₁

9.9

MOLICKA-HANIAWETZ, Anna, mgr inz.; OGAZA, Henryk, mgr inz.

Possibilities of applying collective flotation of zinc-lead
ores. Rudy i metale 6 no.8:352-355 Ag '61.

MOLICKA-HANIAWETZ, Anna, dr inz.; OGAZA, Henryk, mgr inz.

Effect of adding jig tailings in the flotation of ore.
Rudy i metale 9 no.6:297-299 Je '64.

MOLICKA-HANIAWETZ, Anna, dr inz.

Comparison of the Italian and Polish methods of oxidized zinc
mineral flotation. Rudy i metale 9 no.12:661-664 D '64.

GHIEWKOWSKA, H.; KWIECINSKA, K.; MOLIER, S.; TYBOROWSKA, K.

Effect of kindergartens on health, mental development and physical efficiency of children. *Pediat Pol* 37 no.2:151-164 F '62.

1. Z Sekcji Higieny Szkolnej Kierownik: dr M. Rudolf-Skokowska
Instytutu Matki i Dziecka Dyrektor: prof. dr med. F. Groer z Pracowni
Teorii Wychowania Fizycznego Instytutu Naukowego Kultury Fizycznej i
Akademii Wychowania Fizycznego Kierownik: prof. dr med. Z. Gilewicz
i z Katedry Psychologii Wychowawczej UW Kierownik: prof. dr M. Zebrowska.

(CHILD CARE) (SCHOOLS)

SHILKIN, P.M.; ZEL'VYANSKIY, Ya.A.; SIBAROV, Yu.G.; MILOVIDOV, L.G;
KRAPIVIN, V.G.; OZADOVSKIY, I.N.; MOLIN, N.I.;
VOROTNIKOVA, L.F., *tekhn. red.*

[Safety engineering manual for operating the contact networks
of a.c. electrified railroads] Pravila tekhniki bezopasnosti
pri ekspluatatsii kontaktnoi seti peremennogo toka elektrifi-
tsirovannykh zheleznnykh dorog. Moskva, Transzheldorizdat,
1962. 139 p. (MIRA 16:4)

1. Russia (1923-. U.S.S.R.) Glavnoye upravleniye elektrifikatsii
i energeticheskogo khozyaystva. 2. Glavnoye upravleniye elektri-
fikatsii i energeticheskogo khozyaystva Ministerstva putey so-
obshcheniya (for Zel'vyanskiy). 3. Moskovskaya zheleznaya do-
roga (for Milovidov). 4. Gor'kovskaya zheleznaya doroga (for
Krapivin). 5. Vostochno-Sibirskaya zheleznaya doroga (for
Molin). 6. Tsentral'nyy komitet professional'nogo soyuza rabo-
chikh zheleznodorozhnogo transporta (for Sibarov).

(Electric railroads--Wires and wiring)

(Electric railroads--Safety regulations)

MOLIN, V.A.

Spore-pollen complexes in Beloshchel'ye layers of the Tatarian
stage of the Permian in the Mezen' Valley. Trudy Inst.geol.
Komi fil. AN SSSR no.2:47-49 '62. (MIRA 15:7)
(Mezen' Valley--Palynology)

MOLIN, V.A.

Permian vegetation and climate of the Kanin Peninsula according
to spore and pollen analysis. Izv. Komi. fil. Geog. ob-va SSSR
no.8:72-76 '63. (MIRA 17:6)

MOLIN, V.A.

First finds of bivalve *Phyllopodain* in the Indian stage of the
Mangyshlak Peninsula. Paleont. zhur. no.1:84-88 '65. (MIRA 18:4)

1. Institut geologii Komi ASSR, filial AN SSSR.

MOLIN, V. A.

On the Ufa stage in the upper reaches of the Mezen' River.
Dokl. AN SSSR 147 no. 4: 904-905 D '62. (MIRA 16:1)

1. Institut geologii Komi filiala AN SSSR. Predstavleno
akademikom D. V. Nalivkinym.

(Mezen' Valley—Geology, Stratigraphic)

BUDANOV, G.F.; MOLIN, V.A.

Vetluga series of the Triassic of the Mezen' basin. Dokl. AN SSSR
149 no.2:381-384 Mr '63. (MIRA 16:3)

1. Institut geologii Komi filiala AN SSSR. Predstavleno akademikom
D.V.Nalivkinym.

(Mezen' Valley--Geology, Stratigraphic)

MOLIN, V.A.

New conchostracans from the Ufa stage of the Kazan' Valley.
Paleont. zhur. no. 1:76-81 '64. (MIRA 17:7)

1. Komi filial AN SSSR.

MOLIN, V.A.; BUDANOV, G.F.

Permian and Triassic of the Zimino anomaly area in the southwestern
part of the Timan Ridge region. Trudy Inst.geol.Komi fil. AN SSSR
no.3:67-77 '62. (MIRA 16:9)

(Timan Ridge region—Geology, Stratigraphic)

MOLIN, Vladimir Afanas'yevich; NOVOZHILOV, Nestor Ivanovich;
CHERNOV, A.A., prof., doktor geol.-miner. nauk, otv.
red.[deceased]

[Permian and Triassic bivalve branchiopods in the north
of the U.S.S.R.] Dvustvorchatye listonogie permi i
triasa Severa SSSR. Moskva, Nauka, 1965. 116 p.
(MIRA 19:1)

CHALYSHEV, Vasil'y Ivanovich; VARYUKHINA, Liliya Mikhaylovna;
MOLIN, Vladimir Afanas'yevich; PLOTNIKOV, M.A., kand.
geol.-miner. nauk, etc. red.

[Boundary of Permian and Triassic red beds in the northern
part of the cis-Ural region] Granitsa permi i triasa v
krasnetsvetnykh otlozheniyakh Severnogo Priural'ia. Moskva,
Nauka, 1965. 118 p. (MIRA 18:8)

MOLIN, V.A.

Correlation of Lower Triassic sediments in the northern
regions of the U.S.S.R. according to the fauna of bivalve
Phyllopoda. Dokl. AN SSSR 165 no.4:901-903 D '65. (MIRA 18:12)
1. Institut geologii Komi filiala AN SSSR. Submitted June
26, 1965.

MOLIN, YU. N.

AUTHOR

HAZUVAYEV, G.A., SOROKIN, YU. A., DOMRACHEV, G.A., 20-6-30/59
PETUKHOV, G.G., TSVETKOV, YU. D., MOLIN, YU. N.

TITLE

On the structure of organochromic compounds.

PERIODICAL

(O stroynii khromorganicheskikh soedineniy.- Russian)
Doklady Akademii Nauk SSSR 1957, Vol 113, Nr 6, pp 1293-1294
(U.S.S.R.)

ABSTRACT

In a paper recently published by Fischer the synthesis of neutral dibenzolchromium and its salts is described and a report is made concerning some further aromatic derivatives of the chromium-(0). This author assumes that the latter compound has an A-structure analogous to ferrocene. Recently a series of reports was published in which the separation from the reaction products of C_6H_4MgBr and also of the dibenzolchromium with waterless chlorinechromium beside "pentaphenylchromhydroxide" and "tetra" as well as "triphenylchromiodides" is described by Hein. According to a bold, but not precisely proved assumption of Zeiss, the polyphenyl derivatives of chromium have a common bis-aren-structure. If it is assumed that in the chromium iodides (π -benzol, π -diphenyl) and di-(π -diphenyl)-chromium the diphenylgroups are covalently connected, 10 % of D should be expected in the diphenyl separated after the

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reaction with LiAlD_4 . If, however they have a B-structure (illustration 1) diphenyl would contain no deuterium. The composition and the yield of the organic products of the light dispersion of the organochromic compounds in the chloroform agree well with the B-structures. It is known that the compounds of the B-series are paramagnetic and have the magnetic moment = 1.7 of the Bohr magneton. This corresponds to the existence of a not coupled electron in their molecule. Therefore, the photographing of the spectra of the paramagnetic electron-resonance of such compounds was interesting in order to obtain data about the localisation of the free electron. The absorption spectrum of the aqueous solution of one of these substances (III) is shown by illustration 2. The existence of a superfine structure and the qualitative analysis of the intensity distribution shows that the not coupled electron is in interaction with the hydrogen nuclei of the aromatic rings. (2 illustrations, 1 Slavic reference.)

ASSOCIATION: Scientific Research Institute for Chemistry at the Gorkij State University "N.I. LOBACHEVSKIY".
MOSCOW PHYSICAL-TECHNICAL INSTITUTE.
Institute for Chemical Physics of the Academy of Science of the U.S.S.R.

CARD 2/3

SOV/51-5-1-17/19

AUTHORS: Veyevodskiy, V.V., Molin, Ya.I. and Chibrikov, V.M.

TITLE: Electron Paramagnetic Resonance Spectra of Cr-Aromatic Compounds with Various Substituents (Spektry elektronogo paramagnitnogo rezonansa Cr-aromaticheskikh soedineniy s razlichnyimi zamestitel'yami)

PERIODICAL: Optika i Spektroskopiya, 1958. Vol 5, Nr 1, pp 90-92 (USSR)

ABSTRACT: The present note reports continuation of the work described in Ref 1-2 on electron paramagnetic resonance spectra of solutions of $(C_6H_5)_2CrI$, $(C_6H_5 \cdot C_6H_{11})_2CrI$, $(C_6H_5 \cdot C_6H_5)(C_6H_5)CrI$ and $(C_6H_5 \cdot C_6H_5)_2CrI$. These compounds are denoted I, II, III and IV respectively in the present note. The purpose of the work was to find the effect of substitution of the distribution of density of unpaired electrons. Isopropyl alcohol, acetone, pyridine and water were used as solvents. All measurements were made at room temperature using a spectrometer working at 9300 Mc/s. The modulation depth of the magnetic field was 2 Oe. The g-factor, the total line-width in Oe, the separation of the hyperfine structure components (ΔH) and the number of resolved hyperfine structure (h.f.s.) components for the compounds I-IV in isopropyl alcohol are given in the table

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Electron Paramagnetic Resonance Spectra of Cr-Aromatic Compounds with Various Substituents

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on p 91. The consistency of g and ΔH in the series of compounds I-IV indicates that introduction of a substituent into the benzene ring does not materially change the distribution of density of unpaired electrons between Cr and the benzene rings. Improvement of the resolution of the spectrum (see the figure on p 92) on going from the compound I to the compound IV was observed. The authors make the following conclusions. (1) In dilute solutions the h.f.s. component width ceases to depend on concentration below a certain concentration which is different for different solvents. (2) The width of h.f.s. components in dilute solutions depends on the nature of the solvent. (3) On increase of the solution concentration the h.f.s. disappears at different concentrations in different solvents. The main reason for the disappearance of the h.f.s. is the exchange interaction between paramagnetic particles. The authors thank Professor G.A. Razuvaev (Gor'kiy Institute of Organic Chemistry) and Professor F. Hein (Institute of Inorganic Chemistry, Jena, Eastern Germany) for supply of the compounds studied. There are 1 figure, 1 table and 5 references, 3 of which are American and 2 Soviet.

Card 2/2

ASSOCIATION: Institut Khimicheskoy fiziki, AN SSSR (Institute of Chemical Physics, Academy of Sciences of the U.S.S.R.)

SUBMITTED: January 27, 1958 graphic analysis 2. Metalorganic compounds-Magnetic properties 3. Cyclic compounds-Properties 4. Chromium iodine compounds-Properties

MOLIN, YU. N.

AUTHOR: Molin, Yu. N., Voyevodskiy, Y. V.

57-1-19/50

TITLE: Investigation of Action of the Ionizing Radiation on Quartz by the Method of Electron Paramagnetic Resonance (Issledovaniye vozdeystviya ioniziruyushchego izlucheniya na kvarts metodom elektronnoy paramagnitnoy rezonansy)

PERIODICAL: Zhurnal Tekhnicheskoy Fiziki, 1958, Vol. 28, Nr 1, pp. 143-149 (USSR)

ABSTRACT: The investigation of the paramagnetic resonance absorption was carried out on a spectrometer of the Superheterodyn type with 9.300 mc and of a sensitivity of $5 \cdot 10^{14}$ of the diphenylpicrylhydrazil - (DFPH) - radical-particle. (ref. 10, 11.) The samples of the crystalline quartz are produced of rock crystal. The quartz samples were irradiated with γ -rays of Co^{60} . Irradiation and measuring were carried out at room temperature. On the occasion of the investigation of the temperature influence on the behaviour of the defects the samples were heated in the electric furnace (outside of the resonator). Molten quartz which has been irradiated with γ -rays and crystalline quartz irradiated with γ -rays and neutrons were investigated. The molten quartz which had

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Investigation of Action of the Ionizing Radiation on
Quartz by the Method of Electron Paramagnetic Resonance

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not been irradiated gave no signals of paramagnetic absorption. On the occasion of irradiation the quartz became violet and showed two absorption lines. These lines are called α and β signals according to their sequence in the magnetic field. The paramagnetic centres which give the α and β signals are here called α and β defects. The α signal showed no sign of saturation. Saturation of the β signals occurred without change of the signal. Width and shape of the β signal seem to be due to the anisotropy of the g -factor. The shape of the saturation curve of the β -signal was analysed according to the methods described in Ref. 13 and 14 and a value of the order of magnitude of 10^{-5} sek was obtained for the time of the spin-lattice-relaxation T_1 . The investigation of the dependence of the concentration of the α and β -defects on the irradiation dose showed that in the case of doses of an order of magnitude of 10^1 the defect concentration reaches saturation. In the first part of the curve the concentration of the β -defect is proportional to the square root of the irradiation dose. Because of insufficient accuracy of the spectrometer the first section of the curve for the α -effect

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could not be recorded. In accordance with ref. 7 and 8 it could be observed that on the occasion of the heating of the irradiated molten quartz up to 300 and 400°C it turned from violet into blue. The heating was accompanied by changes in the spectrum of the paramagnetic absorption. It could be observed that when the α -signal disappears the β -signal increases simultaneously. The initial concentration of the α -defects is about three times greater than that of the β -defects. The grinding of irradiated quartz into powder does not change the intensity of the α and β -signals. It influences, however, the behaviour of the β -signal on the occasion of heating. Due to the grinding the temperature at which the β -defect disappears changes by 350°. The following was observed on the occasion of the investigation of crystalline quartz:

- 1) The monocrystal gave no signal of paramagnetic absorption after irradiation with γ -rays (10^7 röntgen), neither at room temperature nor at the temperature of liquid nitrogen.
- 2) At the same irradiation fine polycrystalline powder gave a weak signal which as to its shape and position on

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the spectrum was similar to the β -signal in molten quartz. In the case of great amplitudes of the radiation-frequency-field this signal "saturated" like the β -signal.

3) After irradiation by means of a nuclear reactor (γ -rays, neutrons) the monocrystal gave the same signal as in case 2, it was only somewhat more intense. Besides, some weak signals were observed in the range of $g \approx 2$. The dependence of the concentration of the β -defects on the irradiation dose observed here, can be explained by considering the finite number of traps and by taking into consideration that simultaneously with the process of capturing of free electrons and holes through the traps also processes of recombination of free electrons with the captured holes and of the free holes with the captured electrons occur. It is presumed that paramagnetic absorption in irradiated quartz is due to the electrons and holes captured by the structural defects. A simple table is given on the basis of which the fundamental qualitative rules of the accumulation-kinetics of paramagnetic defects can be explained. The behaviour of the α and β -defects on the occasion of heating can equally be explained on the basis

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Quartz by the Method of Electron Paramagnetic Resonance

57-1-19/30

of this model. There are 6 figures, and 14 references,
1 of which is Slavic.

ASSOCIATION: Institute for Chemical Physics AN USSR Moscow
(Institut khimicheskoy fiziki AN SSSR Moskva)

SUBMITTED: May 3, 1957

AVAILABLE: Library of Congress

Card 5/5

5(4)

AUTHORS:

SOV/20-123-5-31/50
Molin, Yu. N., Koritskiy, A. T., Buben, N. Ya., Voevodskiy, V.V.,
 Corresponding Member, Academy of Sciences, USSR

TITLE:

The Investigation of Free Radicals Formed in Solid Bodies in
 the Process of Irradiation by Fast Electrons (Issledovaniye
 svobodnykh radikalov, obrazuyushchikhsya v tverdykh telakh
 v protsesse oblucheniya bystryimi elektronami)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 123, Nr 5, pp 882-883
 (USSR)

ABSTRACT:

The authors endeavored to detect radicals of short life-times
 in solid bodies formed by fast electrons. The present paper
 gives data concerning radicals of life-times of some minutes.
 The authors constructed an apparatus for the immediate re-
 cording of the spectrum of the paramagnetic electron resonance
 during the irradiation of the investigated specimen. Prepara-
 tion of the samples is discussed in short. The experiments
 were carried out at room temperature. The authors observed a
 signal of paramagnetic electron resonance during the irradia-
 tion of the specimen and after the interruption of the irradi-
 ation. More than 20 various substances were investigated,
 namely polymers (polyethylene, nylon, caprone, polymethyl

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The Investigation of Free Radicals Formed in Solid Bodies in the Process
of Irradiation by Fast Electrons

metacrylate, teflon, and various specimens of rubber), solid organic acids and their salts (oxalic acid and their salts, succinic acid and their sodium salt, stearic acid and citric acid), aromatic compounds (naphthalene, α -naphthol, β -naphthol, benzoyl peroxide, metol). In all the investigated samples, the concentration of the radicals reached saturation at doses of some dozens of megarad. In the case of the majority of the investigated substances, the produced radicals were rather stable, their life-time amounted to some hours (in some cases also to longer periods). Some details are given in short. During the irradiation of polyethylene, the authors could record the radical $-\text{CH}_2^{\bullet}-\text{CH}-\text{CH}_2-$ which is not stable at room temperature. The spectrum of this radical is shown in a figure. According to measurements at temperatures below room temperature, the rate of conversion of the primary radical into the second one decreases with a decrease of temperature. There are 1 figure and 1 Soviet reference.

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SOV/20-123-5-31/50

The Investigation of Free Radicals Formed in Solid Bodies in the Process
of Irradiation by Fast Electrons

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR
(Institute of Chemical Physics of the Academy of Sciences,
USSR)

SUBMITTED: August 11, 1958

Card 3/3

KORITSKIY, A.T.; MOLIN, Yu.N.; SHAMSHEV, V.N.; BUBEN, N.Ya.;
VOYEVODSKIY, V.V.

Study of radicals by means of electronic paramagnetic resonance during the irradiation of polyethylene by fast electrons. Vysokom.sped. 1 no.8:1182-1193 Ag '59.
(MIRA 13:2)

I. Institut khimicheskoy fiziki AN SSSR.
(Polyethylene) (Radicals(Chemistry))

TSVETKOV, Yu.D.; MOLIN, Yu.N.; VOYNODSKIY, V.V.

Electron resonance spectra of some irradiated polymers.
Vysokom.sped. 1 no.12:1805-1811 D '59. (MIRA 13:5)

1. Institut khimicheskoy kinetiki i goreniya AN SSSR
(Sibirskoye otdeleniye).
(Polymers--Spectra)

SOV/76-33-7-37/40

5(4)

AUTHORS:

Molin, Yu. N., Tsvetkov, Yu. D.

TITLE:

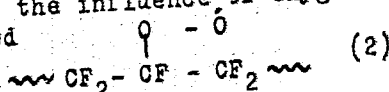
On Changes in the Course of the Lines of Electron Paramagnetic Resonance With Temperature in Radicals of the Peroxide Type

PERIODICAL:

Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 7, pp 1668 - 1670 (USSR)

ABSTRACT:

In the papers (Refs 1,2), the spectra of electron paramagnetic resonance (EPR) of irradiated Teflon were investigated, and it was found that under the influence of oxygen radicals of the peroxide type are formed



Furthermore, it was found that the course of the absorption curve of radical (2) depends largely on temperature. In this article, the authors carried out pertinent investigations at -198° - 150° C. Herefrom it resulted that the asymmetry (A) of the above curve does not change within the temperature ranges -200° - -100° C and 50° - 150° C. Within the range -100° - 50° C the course of the curve changes uniformly and (A) changes its sign at about 50° C. Several measurements showed that the above changes in the course of the curve take place in a reversible manner within the temperature range under investigation. It is

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On Changes in the Course of the Lines of Electron Paramagnetic Resonance With Temperature in Radicals of the Peroxide Type SOV/76-33-7-37/40

therefore assumed that radical (2) does not change its structure within this range. The experimental results obtained may be explained by the assumption that the change in the course with temperature depends on the change of motion of the group -O -O with respect to the C - O bond in radical (2). The authors then give some explanations by means of a simple model under the assumption that at temperatures of above 50°C a free rotation of the -O - O group with respect to the C - O bond takes place. However, these considerations hold only in the first approximation since for a quantitative interpretation of the resultant data the shape and height of the potential barrier for the rotation of the - O - O group must be known. There are 2 figures and 4 references, 1 of which is Soviet.

ASSOCIATION: Akademiya nauk SSSR, Institut khimicheskoy fiziki, Moskva (Academy of Sciences of the USSR, Institute of Chemical Physics, Moscow)

SUBMITTED: August 28, 1958

Card 2/2

5(4)

AUTHORS: Molin, Yu. N., Koritskiy, A. T., SOV/20-124-1-35/69
Buben, N. Ya., Voevodskiy, V. V., Corresponding Member, AS USSR

TITLE: Investigation by the Method of Paramagnetic Electron Resonance of Free Radicals Formed During Irradiation of Oxalic Acid
(Issledovaniye metodom elektronnogo paramagnitnogo rezonansa svobodnykh radikalov, obrazuyushchikhsya pri obluchenii shchhavelevooy kisloty)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 1, pp 127-128 (USSR)

ABSTRACT: The procedure developed by the authors for the purpose of observing free radicals by the method of paramagnetic electron resonance in connection with the action of fast electrons on matter also permits the investigation of the creation and annihilation of radicals in solids. The present paper contains preliminary data concerning the properties of radicals formed by the irradiation of oxalic acid with 1.6 Mev electrons. The signal of paramagnetic absorption in oxalic acid consists of a single line having a width of about 4.5 Oe. The corresponding g-factor is similar to that of diphenyl-picryl hydrazyl (2.0036).

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Investigation by the Method of Paramagnetic Electron Resonance of Free Radicals Formed During Irradiation of Oxalic Acid SOV/20-124-1-35/69

After irradiation has been discontinued, signal intensity decreases at a rate that depends on temperature. A diagram shows one of the curves for the variation of radical concentration, which was plotted at room temperature. In the temperature interval of $+10^{\circ}$ to $+40^{\circ}$ the recombination of radicals is described by the equation $dn/dt = -kn^2$, where n denotes the concentration of the radical and k a temperature-dependent constant. At $+25^{\circ}$ the value $k \approx 9 \cdot 10^{-22} \text{ cm}^3/\text{sec}$ was found by employing the usual methods. According to the quadratic law of recombination it would be expected that, at constant temperature, the steady concentration of radicals after saturation is proportional to the square root of the efficiency per dose of irradiation. A table contains data on the dependence of the steady concentration of the radical on the density of the electron flux. Accumulation of radicals is, however, not described by a simple kinetic equation $dn/dt = w_0 - kn^2$, but it is of complicated character. For the purpose of determining the nature of the radical in oxalic

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Investigation by the Method of Paramagnetic Electron Resonance of Free Radicals Formed During Irradiation of Oxalic Acid SOV/20-124-1-35/69

acid, the authors compared the spectra of the paramagnetic resonance of irradiated oxalic acid, succinic acid, and stearic acid as well as of some of their salts. The following was found: also in the rather complicated spectra of succinic acid and stearic acid signals of paramagnetic resonance occur which are analogous to the signal in oxalic acid. In the spectra of the salts, such signals are either of only weak intensity or they lack entirely. The experimentally determined law of quadratic recombination is indicative of the fact that the radicals are destroyed by the interaction of two radicals. Either the diffusion of a radical in matter by the transition of a hydrogen atom from the neighboring molecule to the radical, or dislocation of a free electron according to the system of conjugate hydrogen bonds may be considered as possible mechanisms. Further investigations are necessary for the purpose of determining the true mechanism. There are 2 figures, 1 table, and 2 Soviet references.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute
Card 3/4 for Chemical Physics of the Academy of Sciences, USSR)

Investigation by the Method of Paramagnetic Electron Resonance of Free Radicals Formed During Irradiation of Oxalic Acid SOV/20-124-1-35/69

SUBMITTED: August 11, 1958

Card 4/4

5-4) 5.4300, 5.4130

AUTHORS:

Molin, Yu. N., Sharpatyy, V. A.,
Buben, N. Ya.

66431

SOV/20-128-6-36/63

TITLE:

The Electron Paramagnetic Resonance Spectra and Kinetics of Accumulation of Radical Products Forming When Frozen Aqueous Solutions of Sodium Nitrate Are Bombarded With Fast Electrons

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 6, pp 1224 - 1227 (USSR)

ABSTRACT:

By means of the apparatus described in reference 7 for the investigation of spectra of electron paramagnetic resonance (epr) the epr + spectra of frozen aqueous solutions of NaNO_3 were photographed at -145°C (Fig 1). The characteristics of the spectra of radicals I - IV are given in table 1. Radical I is identified as NO_2 , radical II as the ion HNO_3^- . Radical III was observed in acid medium, radical IV in alkaline medium only. These two radicals are called nitrogen-free peroxide radicals, but they have not yet been clearly identified. Figure 2 shows the radical yield G_R as a function of the concentration of NaNO_3 . It indicates that the reaction mechanism is not affected by the

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The Electron Paramagnetic Resonance Spectra and Kinetics of Accumulation of Radical Products Forming When Frozen Aqueous Solutions of Sodium Nitrate Are Bombarded With Fast Electrons

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concentration and that the indirect effect of the irradiation prevails in it. This is also confirmed by the difference between the epr spectrum of solid NaNO_3 and that of its solution. In order to clarify the role of the radicals in the formation of NO_2^- the yields G_R and $G_{\text{NO}_2^-}$ are compared with each other in

table 2. The striking sensibilizing effect of the alkaline medium which can be found in this comparison needs further detailed investigation. The authors thank V. N. Shamshev and A. T. Koritskiy for their cooperation in the experiments, and V. V. Voyevodskiy, Corresponding Member of the AS USSR, Professor M. A. Proskurnin and V. D. Orekhov for valuable advice. There are 2 figures, 2 tables, and 18 references, 8 of which are Soviet.

ASSOCIATION:

Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemicophysics of the Academy of Sciences, USSR). Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova (Scientific Research Institute of Physical Chemistry imeni L. Ya. Karpov)

Card 2/2

86745

5-5800(1043, 1227, 1273)

S/120/60/000/006/020/045

E032/E314

AUTHORS: Molin, Yu.N., Koritskiy, A.T., Semenov, A.G.,
Buben, N.Ya. and Shamshev, V.N.

TITLE: Apparatus for the Observation of E.P.R. Spectra of
Solids During Their Irradiation by Fast Electrons

PERIODICAL: Pribery i tekhnika eksperimenta, 1960, No. 6,
pp. 73 - 77

TEXT: The electron paramagnetic resonance method (E.P.R.)
is being widely used to study the properties of radicals in
materials subject to ionising radiation. Usually, such
studies are carried out in two stages. In the first stage,
the sample is irradiated and in the second the E.P.R. spectrum
is recorded. This method is not always convenient because it
cannot be used to determine short-period processes taking place
in the specimen. In order to remove this disadvantage the
present authors have designed an apparatus in which the specimen
can be irradiated in situ in the E.P.R. spectrometer. The
E.P.R. spectrometer, employing a high-frequency modulation of
the magnetic field and working on a wavelength of about 3.2 cm,
was described in detail by Semenov and Bubnov in Ref. 5. The
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E032/E314

Apparatus for the Observation of E.P.R. Spectra of Solids
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absorbing cell in the spectrometer is in the form of an H_{012} rectangular resonator with a Q-factor of about 1 000. The source of the ionising radiation was the electron accelerator of the Institute of Chemical Physics of the AS USSR, which gives electrons of up to 2 MeV in energy. Fig. 1 shows the method of introducing the electron beam into the resonator of the spectrometer. The electrons are introduced through a cylindrical channel in one of the pole pieces of the magnet so that they enter along the lines of force. The presence of the channel, whose diameter on the pole-piece face is 6 mm, leads to a deterioration in the uniformity of the magnetic field. The nonuniformity at the specimen was found to be 0.8 Oe/cm in the direction of the axis of the channel but very small in the perpendicular direction. Since usually the E.P.R. line width in solids is of the order of 10 Oe, such a nonuniformity does not reduce the resolution of the spectrometer when the thickness of the specimen is of the

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order of 1 or 2 mm. The entire apparatus is placed in a special enclosure which screens it from X-rays. In the region in which the radiation strikes the specimen, there is only the magnet, the resonator and the high-frequency field modulator. The constant magnetic field and the modulation fields are adjusted by remote control. The power is introduced into the resonator through rectangular waveguides having a total length of about 25 m. These had practically no effect on the sensitivity and stability of the spectrometer. The electron-beam current was monitored by an ionisation chamber (5 in Fig. 1) which was placed above the specimen 8. Additional magnets were provided for controlling the beam. The ionisation chamber was in the form of two foils, each 5 μ thick, and separated by a gap of 5 mm. Ions produced in the gap between the foils are extracted by an electric field derived from a storage battery of 160 V. The dose delivered to the specimen was determined from the formula:

X

$$D = AIt$$

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where I is the electron current in μA at the beam shutter
4 (Fig. 1),

t is the time of irradiation and

A is a constant for the given substance.

The latter constant is given by:

$$A = \frac{dE}{d\xi} n \frac{j}{I},$$

where $dE/d\xi$ is the rate of loss of energy in the

irradiated specimen in eV/g/cm^2 ,

n is the number of electrons in $1 \mu\text{A}$ of beam
current,

j/I is the ratio of current densities at the beam
shutter and at the specimen.

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The constant A was determined in special experiments in which the specimen was replaced by special probes having the same dimensions as the specimen. In the measurements reported in the present paper the dose rate was varied between 3×10^6 and 3×10^3 rad/sec. The temperature of the specimen was varied by blowing a stream of nitrogen from a dewar filled with liquid nitrogen. In this way, any temperature between -150 and $+150$ °C can be obtained to within ± 1 °C. The specimens were in the form of discs 3 or 5 mm in diameter and 2 mm thick. The discs were placed in the resonator at the end of a thermocouple. Acknowledgments are expressed to V.V. Voyevodskiy for his interest in the present work. There are 7 figures and 7 references: 6 Soviet and 1 English.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR
(Institute of Chemical Physics of the AS USSR)

SUBMITTED: November 12, 1959

Card 5/5

5.3100
5.4500(B)

67899

5(+)

AUTHORS:

Chkheidze, I. I., Molin, Yu. N.,
Buben, N. Ya., Voyevodskiy, V. V.,

S/020/60/130/06/031/059
B004/B007

Corresponding Member AS USSR

TITLE:

The E.P.R.-Spectra¹ and the Kinetics of the Accumulations of
Radicals¹ in the Radiolysis of Some Aromatic Compounds

PERIODICAL:

Doklady Akademii nauk SSSR, 1960, Vol 130, Nr 6, pp 1291 - 1293
(USSR)

ABSTRACT:

It was the aim of the present paper to determine the nature of the radicals formed in the radiolytical decomposition of aromatic hydrocarbons, as well as to investigate the influence exerted by structure upon the yield of radicals. The electron paramagnetic resonance (e.p.r.) - spectra of the radicals were recorded which are formed under the influence of fast electrons (1.6 Mev), and the kinetics of their accumulation was measured. Irradiation was carried out at -124 and at +33°. Chemically pure benzene¹ was used. The other compounds: diphenyl, p-ditolyl, o-ditolyl, m-terphenyl, and p-terphenyl were supplied by the laboratory of K. P. Lavrovskiy of the Institut neftekhimicheskogo sinteza (Institute of Petroleum-chemical Synthesis). Figure 1 shows the e.p.r. spectra at -124°. The e.p.r. spectrum

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The E.P.R.-Spectra and the Kinetics of the
Accumulations of Radicals in the Radiolysis of
Some Aromatic Compounds

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B004/B007

of benzene shows a well resolved triplet, the central component of which is, however, considerably more intense than corresponds to the binomial law. This is explained by the superposition of the triplet and a single line. The triplet is ascribed to the radical C_6H_5 , the unpaired electron of which enters into interaction with the adjacent H-atoms. The low yield in molecular hydrogen leads to the conclusion that the H-atoms mostly join the benzene ring, forming the radical C_6H_7 , which produces the single line. The superfine structure of the e.p.r. spectrum of benzene becomes more distinct with rising temperature. This is explained by the quickening of the inhibited rotation round the axis of the sixth order, the existence of which was detected in the course of the investigation of nuclear resonance. The components of the e.p.r. spectra of terphenyls and ditolyls are also triplets, but they are not so distinctly resolved. These spectra are explained by the detachment of hydrogen atoms or CH_3 -groups in para position to

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Some Aromatic Compounds

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B004/B007

the phenyl substituent, where the detached H or CH_3 again joins on the benzene ring, similar to the case of the radical C_6H_7 .

The low resolution of the polyphenyl spectra is explained by delocalization of the unpaired electron. Table 1 shows the radical yields, figure 2, the kinetics of the accumulation of radicals. The low radical yields of ditolyls and terphenyls as against benzene agree with published data on the greater stability of polyphenyls (Ref 9). As regards the isomer yields, the differences found are within the error limits. The authors thank A. M. Brodskiy and V. B. Titov for the polyphenyls placed at their disposal and for discussing the results obtained, and they further thank V. N. Shamshev for taking part in the experiments. There are 2 figures, 1 table, and 13 references, 4 of which are Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of
Chemical Physics of the Academy of Sciences, USSR). Institut
khimicheskoy kinetiki i gorennya Sibirskogo otdeleniya AN SSSR.

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3

5.4500(B)

68820

AUTHORS: Molin, Yu. N., Chkheidze, I. I., S/020/60/131/01/035/060
 Petrov, A. A., Buben, N. Ya., B004/B011
 Voyevodskiy, V. V., Corresponding Member AS USSR

TITLE: Investigation of Processes of Energy Transfer in the Radio-
 lysis of Certain Frozen Hydrocarbons by the E.P.R. Method

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 131, Nr 1, pp 125 - 128
 (USSR)

ABSTRACT: The authors investigated the energy transfer in the compounds
 1,1-dicyclohexyl dodecane (I), 1,1-diphenyl dodecane (II),
 1-phenyl-1-cyclohexyl dodecane (III), which were irradiated
 with fast electrons (1.6 Mev), mixtures from I and II (1 : 1),
 as well as cyclohexane and benzene at -120° . The points of
 rupture in the chemical bonds were determined by taking the
 spectrum of electron paramagnetic resonance (E.P.R.). Further-
 more, the energy transfer to the aromatic ring in compounds II
 and III was to manifest itself in a decrease of the yield in
 radicals due to the protective effect of the aromatic ring.
 Apparatus, method, and synthesis of compounds I - III had al-
 ready been described in references 8 - 9. Figures 1,2 show the
 E.P.R. spectra taken at ~ 9400 megacycles. In the benzene ring

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Investigation of Processes of Energy Transfer in S/020/60/131/01/035/060
the Radiolysis of Certain Frozen Hydrocarbons by B004/B011
the E.P.R. Method

alone, a rupture of the chemical bond occurred in the case of the molecules of compounds II and III. As a consequence, there occurred an energy transfer to the ring. Figure 3 shows the kinetics of the accumulation of radicals. Compounds with benzene ring exhibited no deviation from linearity up to 100 Mrad, whereas in the case of I and cyclohexane, deviations occurred already with a radiation dose of 10 - 30 Mrad. The yield G_R on radicals is shown in table 1. G_R is lower in the case of compounds with benzene ring. The lower value of G_R in the case of a mixture of I and II indicates energy transfer from I to II. The almost trebled value of G_R for II and III as compared to benzene gives evidence of the lower stability of the substituted benzene ring. The authors thank G. K. Voronova for her cooperation. There are 3 figures, 1 table, and 11 references, 6 of which are Soviet.

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Investigation of Processes of Energy Transfer in S/020/60/131/01/035/060
the Radiolysis of Certain Frozen Hydrocarbons by B004/B011
the E.P.R. Method

ASSOCIATION: Institut khimicheskoy kinetiki i goreniya Sibirskogo otdeleniya
Akademii nauk SSSR (Institute of Chemical Kinetics and Com-
bustion of the Siberian Department of the Academy of Sciences,
USSR). Institut khimicheskoy fiziki (Institute of Chemical
Physics). Institut geologii i razrabotki goryuchikh iskopayemykh
Akademii nauk SSSR (Institute of Geology and Mining of Com-
bustible Minerals of the Academy of Sciences, USSR)

SUBMITTED: November 4, 1959

Card 3/3

54600

33101
S/638/61/001/000/026/056
B104/B138

AUTHORS: Molin, Yu. N., Chkheidze, I. I., Petrov, A. A., Buben, N. Ya.,
Voyevodskiy, V. V.

TITLE: Investigation of energy transfer processes during the
radiolysis of congealed hydrocarbons, by the paramagnetic
electron resonance method

SOURCE: Tashkentskaya konferentsiya po mirnomy ispol'zovaniyu
atomnoy energii. Tashkent, 1959. Trudy, v. 1. Tashkent,
1961, 178 - 181

TEXT: The following compounds were investigated: (I) 1,1-dicyclohexyl
dodecane; (II) 1,1-diphenyl dodecane; (III) 1-phenyl 1-cyclohexyl
dodecane. The energy transfer during radiolysis was determined by means
of paramagnetic electron resonance, and from the total radiation yield.
Paramagnetic electron resonance spectra were taken of compounds I - III,
and of benzene and cyclohexane. The substances were irradiated with
1.6-Mev electrons at -120°C. The spectra were taken during irradiation
with electrons. The cyclohexyl radical, RC_6H_{10} , was primarily formed when

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Investigation of energy transfer...

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irradiating compound I. Radicals are also formed by breaking C-H bonds. The spectra of the irradiated compounds II and III are equal, and similar to that of benzene. Two radicals are formed: the first by the removal of an H atom from the benzene ring, the second by addition of an H atom to a benzene ring. When irradiating a mixture of compounds I and II, radicals are mainly formed from molecules of compound II. In molecules of compounds II and III, it is mainly the bonds in the benzene rings which are broken. In compound I, the first rupture of C-H bonds may be accompanied by a reaction of the H atom, which then permits the formation of radicals. The production of radicals is linearly dependant on irradiation. The yield of radicals in compounds II and III is one order of magnitude smaller than that of compound I. The nearly equal yields of radicals of compounds II and III prove that the energy is transferred to the benzene ring. The yield of radicals in compounds II and III is almost three times that in benzene. This decrease in stability is explained by rupture of the symmetry of the benzene ring. There are 3 figures, 1 table, and 9 references: 4 Soviet and 5 non-Soviet. The four most recent references to English-language publications read as follows: Smaller B., Matheson M. S., J. Chem. Phys., 28, 1169, 1958; Alger R. S.

Card 2/3

Investigation of energy transfer...

Anderson T. H., Webb L. A. J. Chem. Phys., 30, 695, 1959; Rad. Res. 3,
1, 1955; Andrew E. R., Eades R. G. Proc. Roy. Soc., 216A, 398, 1953.

ASSOCIATION: Institut khimicheskoy kinetiki i goreniya Sibirskogo
otdeleniya AN SSSR (Institute of Chemical Kinetics and
Burning of the Siberian Department AS USSR)

33101
S/638/61/001/000/026/056
B104/B138

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S/081/62/000/002/012/107
B149/B102

AUTHORS: Sharpatyy, V. A., Molin, Yu. N

TITLE: Electron paramagnetic resonance spectra and kinetics of the accumulation of products formed during radiolysis of frozen aqueous solutions of sodium nitrate

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 2, 1962, 79, abstract 2B563 (Tr. Tashkentsk. konferentsii po mirn. ispol'zovaniyu atomn. energii, 1959, v. I. Tashkent, AN UzSSR, 1961, 364 - 370)

TEXT: Data are presented which were obtained from studies of electron paramagnetic resonance spectra and kinetics of the accumulation of radiolytically produced radicals formed in frozen solutions of sodium nitrate on their irradiation with accelerated electrons under various conditions. In the process of radical formation, an indirect effect of radiation is the predominant mechanism. Data on the kinetics of accumulation of transition and of final products in the transformation of the system nitrate - water are correlated. [Abstracter's note: Complete translation.]
Card 1/1

MOLIN, Yu.N.; CHKHEIDZE, I.I.; BUBEN, N.Ya.; VOYEVODSKIY, V.V.

Electron paramagnetic resonance spectra of irradiated dicarboxylic acids. Zhur.strukt.khim. 2 no.3:293-300 My-Je '61. (MIRA 15:1)

1. Institut khimicheskoy fiziki AN SSSR i Institut khimicheskoy kinetiki i gorennya Sibirskogo otdeleniya AN SSSR.
(Acids, Organic--Spectra)

5.4500

1273, 1320 1360 1138, 1160

21768

S/195/61/002/002/002/004
B101/B208

AUTHORS:

Molin, Yu. N., Chkheidze, I. I., Buben, N. Ya., Voevodskiy, V. V.

TITLE:

Study of energy transfer to aromatic groups by epr in the radiolysis of organic compounds

PERIODICAL:

Kinetika i kataliz, v. 2, no. 2, 1961, 192-196

TEXT: In Ref. 1 (Dokl. AN SSSR, 131, 125, 1960) the authors have shown by means of epr that in the radiolysis of phenyl-substituted saturated hydrocarbons an energy transfer takes place from the saturated groups to the benzene ring. The present paper gives a preliminary survey on studies carried out on different molecules of the A-D type (A = aromatic energy acceptor, D = radiation-unstable substituent). The compounds studied were synthesized in the laboratory of A. D. Petrov, Corresponding Member AS USSR. Measurements were made on an 3WP-2 (EPR-2) apparatus of the first association, by means of 1.6 Mev electrons. The radiochemical yield G of radicals was determined from the linear initial section of the accumulation curve. The accumulation of radicals was linear up to a concentration $\sim 10^{20} \text{ g}^{-1}$.

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Study of ...

The integral dose was varied from 10 to 200 Mrad, the dose rate from 0.03-0.3 Mrad/sec. Irradiation and measurement were performed at 90-160°K. In some cases, "foreign" epr signals were observed at lower doses, whose intensity was $\sim 10^{18}$ spins/g. This is exemplified in Fig. 1 on the epr spectrum and the accumulation curve for o-ditolyl. The foreign signals are attributed to impurities. Their appearance may give rise to considerable discrepancy of the experimental data at different doses. The G values of several compounds are given in a table:

Compound	G, 1/100 ev	
Paraffin, polyethylene, cyclohexane,		
compounds of the class $\text{H} \text{---} \text{H} \text{---} \text{R}$	~ 5	
Cyclohexyl-hexine, cyclohexyl-acetylene	~ 4	
benzene	0.23	0.04
phenyl acetylene	0.09	
diphenyl	0.045	
p-terphenyl	0.045	

The following conclusions may be drawn: 1) For saturated hydrocarbons and

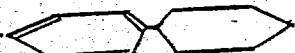



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B101/B208

Study of ...

hydrocarbons with a double or triple bond the G values differ little and amount to several radicals per 100 ev of energy absorbed. 2) In aromatic hydrocarbons without saturated substituents G is by 1-2 orders of magnitude smaller than in saturated hydrocarbons. 3) The radiation stability of aromatic hydrocarbons increases with the degree of conjunction and seems to approach a limit. This also results from G for the following series:

Compound	G, 1/100 ev
	0.55
	0.2
	0.07
	0.045

The difference of G for aromatic and non-aromatic hydrocarbons permits to





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Study of ...

estimate the probability of energy transfer in a complicated AD molecule by measuring the G_{AD} : $G_{AD} = G_A(\gamma_A + \alpha\gamma_D) + G_D\gamma_D(1 - \alpha)$ (1), where G_A , G_D is the radiation yield of the radicals from the groups A and D, γ_A , γ_D are the electron parts of these groups, α the probability of energy transfer from D to A. At $\alpha = 0$, additivity occurs: $G = G_A\gamma_A + G_D\gamma_D$ (2). The probability of energy transfer is calculated from equation (1): $\alpha = [(G_A\gamma_A + G_D\gamma_D) - G_{AD}] / (G_D - G_A)\gamma_D$ (3). The following classes of compounds were studied:

I. -R; R = CH₃, C₂H₅, cycl-C₆H₁₁; II. -(CH₂)_nSiR₃; R = CH₃, n = 0, 1, 2, 3; R = C₂H₅, n = 0 and 3. III: -R and R'--R, where R, R' denotes a saturated hydrocarbon chain, a chain with a double bond, or with a CO group (number of C atoms up to 8). α , calculated by Eq. (3) was between 0.65-0.95. No systematic difference of α was found for the three classes. Fig. 2 shows their epr spectra. Classes I and II (Figs. 26, 24) mainly show lines corresponding to a cleavage of C-H bonds in the benzene ring. Class III (Fig. 22) shows a more complicated spectrum. In the case of long chains of

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5

21768

S/195/61/002/002/004

B101/B208

Study of ...

the substituent lines predominate which are assigned to a bond cleavage in the substituent.. This may be explained by the fact that at $\alpha < 1$ a C-H bond cleavage in the ring becomes less probable than in the radical in spite of energy transfer, owing to a larger stability of the diphenyl group. The small difference between the spectra of I and II and that of benzene (Fig. 2a) is presumably due to the fact that a) the broad spectra of the alkyl radicals form only a background, or b) the stability of the C_6H_6 ring decreases on substitution. This problem has still to be clarified. The authors express their gratitude to Ye. D. Kaplan, Ye. A. Chernyshev, V. F. Mironovich, of the Institut organicheskoy khimii AN SSSR (Institute of Organic Chemistry, AS USSR) for the synthesis of compounds, to G. K. Voronova for her cooperation. There are 2 figures, 1 table, and 5 references: 3 Soviet-bloc and 2 non-Soviet-bloc. The reference to English language publication reads as follows: N. K. Bridge, Nature, 185, 30, 1960.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics, AS USSR) Institut khimicheskoy kinetiki i gorennya SO AN SSSR (Institute of Chemical Kinetics and Burning of the Siberian Department, AS USSR)

Card 5/75

11.1510

30919
S/195/61/002/003/004/009
E030/E452

AUTHORS: Molin, Yu.N. and Yermolayev, V.K.

TITLE: The causes of the change in proton relaxation time
during irradiation of aqueous solutions

PERIODICAL: Kinetika i kataliz, v.2, no.3, 1961, 358-361

TEXT: Hitherto the decrease in relaxation times have been attributed to the formation of free radicals, but calculation shows that improbably high concentrations, 10^{17} to 10^{18} g⁻¹ would be necessary to give the size of effect observed. The present work therefore resolves this question by irradiating solutions of hydrogen peroxide and also distilled water, hexane, benzene and solutions of benzoyl peroxide in benzene, and aqueous solutions close in concentration to those used previously by V.M.Vdovenko and V.A.Shcherbakov (Ref.2: Dokl. AN SSSR, v.127, 127, 1959), and observing simultaneously the NMR signal and also the EPR signal, the latter indicating the formation of any paramagnetic bodies, including free radicals. The apparatus consists of an EPR magnet, with a hole drilled through one pole, to admit a beam of fast (1.6 MeV) electrons. The specimen is held in a glass ampule, diameter 7 mm and volume 0.25 cm³, which is located close to the Card 1/3

30919

S/195/61/001/003/004/009

E030/E452

The causes of the change ...

opposite pole to minimize the field inhomogeneity due to the hole. The NMR field coils are wound on a former which slides over the ampule. The NMR signal is calibrated with standard CuSO_4 solutions with Cu^{++} concentrations of $\sim 10^{17} \text{ cm}^{-3}$; the sensitivity is rather less than in previous work because of the increased field inhomogeneity. The specimen of 30% stabilized impurified H_2O_2 was irradiated at $6 \times 10^4 \text{ rad/sec}$ and after 2 min the amplitude of NMR signal, which had increased rapidly within seconds, reached a high steady value, equivalent to $4 \times 10^{19} \text{ ions Cu}^{++} \text{ cm}^{-3}$. On removal of the irradiation, the signal fell over some 30 min to about one third this value and then appeared constant. It was remarkable that all this time there was no observable change in the EPR signal, thus precluding the formation of a significant concentration of free radicals. Similar results were not obtained with the other solutions. The only plausible explanation of the results is that the relaxation time is decreased by supersaturation into free oxygen, which is known to be formed on irradiation of hydrogen peroxide; this is confirmed by the lack of signal in the other solutions indicating that not more than about 10^{17} cm^{-3} free radicals could remain undetected, and by the failure of the signal to revert to its initial small value in H_2O_2 as should have

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309.9
S/195/61/002/003/004/009
EO30/E452

The causes of the change ...

occurred if formation of free radicals were the operative mechanism. Acknowledgments are expressed to V.V.Voyevodskiy and N.Ya.Buben for their interest in the work. There are 2 figures and 9 references: 6 Soviet and 3 non-Soviet. The references to three English language publications read as follows:

Ref.1: W.T.Duffy, Bull. Amer. Phys. Soc., II, v.4, 250, 1958;

Ref.8: J.G.Marshall, P.V.Rutledge, Nature, v.184, 2013, 1960;

Ref.9: G.Chiarotti, L.Guilotto, Phys. Rev., v.93, 1241, 1954. ✓

ASSOCIATIONS: Institut khimicheskoy fiziki AN SSSR
(Institute of Chemical Physics AS USSR)
Institut khimicheskoy kinetiki i goreniya SO AN SSSR
(Institute of Chemical Kinetics and Combustion SO
AS USSR)

SUBMITTED: October 31, 1961

Card 3/3

5.4600

31088
S/195/61/002/004/002/008
E142/E585

AUTHOR: Molin, Yu.N.

TITLE: The role of the reactions of hydrogen atoms during radiolysis

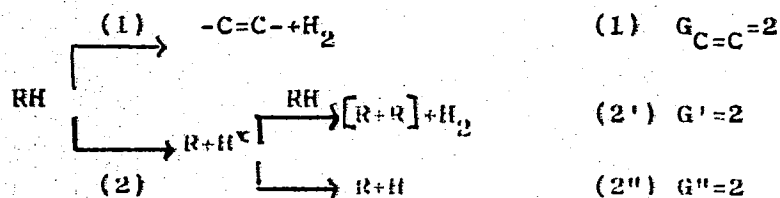
PERIODICAL: Kinetika i kataliz, v.2, no.4, 1961, 490-491

TEXT: The reaction of "hot" and thermal hydrogen atoms during radiolysis in the liquid and solid phases is considered. The rate of radiolysis of organic compounds decreases on transition from the liquid to the solid phase. A comparison of data obtained by the EPR method and by the method of radical-acceptors indicates that the radiation from the radicals also decreases during this process. The authors suggest that a change in the direction of the reactions of hydrogen atoms constitutes one of the main causes of this phenomenon. The radiolysis of straight-chain hydrocarbons was investigated. Experimental data on the formation of hydrogen are most satisfactorily depicted by the following scheme (this type of scheme was investigated by H.A.Dewhurst for the radiolysis of n-pentane (Ref.1: J.Phys.Chem.62, 15, 1958):

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The role of the reactions of ...

31088
S/195/61/002/004/002/004
E142/E585



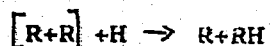
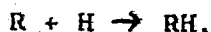
where (1) represents the intramolecular splitting off of hydrogen with the formation of an olefin; (2) represents the breaking of the C-H bond with formation of an alkyl radical R and a "hot" hydrogen atom H^{\bullet} . The "hot" hydrogen either tears off a hydrogen atom from the adjacent molecule which leads to the formation of two closely grouped alkyl radicals (R+R) (this type of reaction with subsequent rapid recombination of the radicals is assumed to explain the joining of polymers (cf. B. A. Medvedev, S. S. Medvedev, Tr. Vsesoyuzn. konf. po radiatsionnoy khimii, M., 1958, p. 209) or it depends on energy during the collisions and becomes thermal. The radiations $G_{C=C}$, G' and G'' , evaluated by other authors, and

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The role of the reactions of ...

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also those calculated in the present investigation (from experimental data, published in literature) show satisfactory agreement within the limits of approximately ± 0.5 . During transition from the solid to the liquid state the conditions of utilization of thermal hydrogen, obtained during process (2"), change substantially. High concentration of the alkyl radicals, which generally recombine rapidly only at a temperature near the melting point of the substance, occurs during the radiolysis of solid hydrocarbons (Ref.3: V. K. Yermolayev, Yu.N.Molin, N.Ya. Buben, Tr.II Vsesoyuzn, soveshch. po radiatsionnoy khimii (in press)). Under these conditions thermal hydrogen, which readily diffuses in hydrocarbons even at the temperature of liquid nitrogen, recombines with R according to the reaction



and does not give additional radiolysis products. This is in contrast to the liquid phase where the fixed concentrations of

Card 3/4

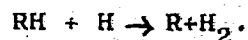
31088

The role of the reactions of ...

S/195/61/002/004/002/008

E142/E585

radicals is very small and the following reaction takes place in general:



Therefore the yield of the radicals and of the radiolysis products must increase substantially. Analogous considerations apply to any hydrogen-containing compounds but the ratio of yields of the reactions of "hot" and thermal hydrogen will finally change in relation to the nature of the molecule. The author expresses his gratitude to V. V. Voyevodskiy for discussing the work. There are 3 references: 2 Soviet-bloc and 1 non-Soviet-bloc. The English-language reference is quoted in the text.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR
(Institute of Chemical Physics, AS USSR)

SUBMITTED: October 31, 1960

Card 4/4

5-4600

26336
S/076/61/035/007/005/019
B127/B102

AUTHORS: Sharpatyy, V. A. and Molin, Yu. N.

TITLE: Electron paramagnetic resonance spectra and kinetics of accumulation of products formed during radiolysis of frozen aqueous sodium nitrate solutions

PERIODICAL: Zhurnal fizicheskoy khimii, v. 35, no. 7, 1961, 1465-1473

TEXT: The authors studied the reactions taking place during radiolysis by means of an e.p.r. spectrometer, using dose rates between $3 \cdot 10^3$ - $3 \cdot 10^6$ r/sec. ^{60}Co with an activity from 30 to 18,000 g-eq. Ra was used as emitter. In order to identify the resonance lines and to study the mechanism of radiolysis the radiolysis of sodium nitrate with admixtures of oxygen, glycerol, ethanol and other alkaline salts was also studied. The working temperature was -145°C . The spectra did not change with changing concentration of the nitrate solution ($2 \cdot 10^{-3}$ -5M). At this temperature the mobility of the radicals formed from water is high enough to enable them to react with the solutes. The radicals formed in radiolysis are stable. In alkaline and

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Electron paramagnetic resonance ...

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S/076/61/035/007/005/019
B127/B102

neutral solutions at least three radicals were detected. Radicals I and II are formed from NO_3^- . (Radical I: NO_2^\cdot . Radical II: HNO_2^\cdot .) Substitution of H by D decreases the width of the line of II. An interaction of the unpaired electrons of II with the surrounding protons apparently affects the line width. The line of II disappears in acid solution; it is not observed in solutions with NO_2^- . A line observed having triplet structure could not be identified with certainty but is assigned to NO_2^\cdot . In neutral and acid NaNO_3 solutions the spectrum of a radical IV was observed. The line of the radical V is only found in alkaline solutions. IV is assumed to be a peroxide radical formed from: $\text{NO}_3^- + \text{OH}^- \rightarrow \text{HON}(\text{OO}^\cdot)$. OH is taken from the water.

The broad line of V might be indicative of hydrated O_2^\cdot . IV disappears when ethanol or glycerol are added to the sodium nitrate solution. A single line with a g-factor of 2.04 appears in the presence of O_2 in NaNO_2 :

$\text{H} + \text{O}_2 = \text{HO}_2^\cdot$. In neutral medium this radical will react with the solutes,

in alkaline solution the following reaction will take place:

$\text{HO}_2^\cdot + \text{OH}^- = \text{O}_2^\cdot + \text{H}_2\text{O}$. In view of the lack of experimental data IV and V

could not be identified with certainty. A direct effect of irradiation on

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Electron paramagnetic resonance ...

26336

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B127/B102

the solutes was not found, but a sensitizing effect of the admixtures. By addition of glycerol or alcohol the yield of radicals could be increased by 40%. The sensitizing effect may be compensated by the tendency of the radicals to recombine to water. The yield of molecular H_2 at liquid-nitrogen temperature was 0.15 molecule/100 ev in pure frozen water. Obviously, the atomic H is then sufficiently mobile either to recombine or to react with the solutes. Other radicals formed in irradiation of ice (especially OH) are stable only down to $-160^{\circ}C$. Dissolved carbon dioxide seems to stabilize H. The yield of radicals and nitrite ions is about the same. The radical yield does not depend on the nature of solutions being saturated with gas. Alkaline solutions exert a sensitizing effect on the radical formation. Mention is made of M. A. Proskurnin, N. Ya. Buben, V. I. Smirnova, T. A. Simonova, V. V. Voyevodskiy. There are 3 figures, 2 tables, and 10 references: 6 Soviet and 4 non-Soviet. The two most important references to English-language publications read as follows: C. K. Yen, et. al.: Phys. Rev., 112, 1169, 1958. L. H. Piette, et. al.: J. Chem. Phys., 30, 1623, 1959.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova
(Physicochemical Institute imeni L. Ya. Karpov)

Card 3/4

S/844/62/000/000/021/129
D244/D307

AUTHORS: Sharpatyy, V. A. and Molin, Yu. N.

TITLE: Radiolysis of $\text{HON}(\text{SO}_3\text{K})_2$ solutions

SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Itd-vo AN SSSR, 1962, 141-143

TEXT: Electron paramagnetic resonance was used to study the kinetics of product formation in the liquid phase radiolysis of $\text{NO}(\text{SO}_3\text{K})_2$ and $\text{HON}(\text{SO}_3\text{K})_2$, the latter giving $\text{NO}(\text{SO}_3\text{K})_2$ on irradiation. In the presence of a competing acceptor, glycerine, the yield of $\text{NO}(\text{SO}_3\text{K})_2$ decreases sharply as compared with the yield obtained on the irradiation of $\text{HON}(\text{SO}_3\text{K})_2$ without glycerine, or in the presence of a conjugated acceptor (nitrate ion). The latter acceptor acts, therefore, as a sensitizer. The formation of $\text{NO}(\text{SO}_3\text{K})_2$ passes through a maximum in a number of cases. The formation of H_2 and O_2

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Radiolysis of $\text{HON}(\text{SO}_3\text{K})_2$...

S/844/62/000/000/021/129
D244/D307

during the irradiation proceeds linearly in the dosage of 0 to 10^5 rads, the yield of the gases depending on the nature of the acceptor. It is concluded that $\text{NO}(\text{SO}_3\text{K})_2$ results from the interaction of hydroxylaminesulphonate-ion with OH radicals. There are 3 figures.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova; Institut khimicheskoy fiziki AN SSSR (Physico-Chemical Institute im. L. Ya. Karpov; Institute of Chemical Physics, AS USSR)

Card 2/2

TOLKACHEV, V.A.; MOLIN, Yu.N.; CHKHEIDZE, I.I.; BUBEN, N.Ya.;
VOYEVODSKIY, V.V.

Electron paramagnetic resonance spectrum of frozen irradiated
benzene. Dokl. AN SSSR 141 no.4:911-912 D '61. (MIRA 14:11)

1. Institut khimicheskoy fiziki AN SSSR i Institut khimicheskoy
kinetiki i goreniya Sibirskogo otdeleniya AN SSSR. 2. Chlen-kor-
respondent AN SSSR (for Voyevodskiy).
(Benzene—Spectra)

S/844/62/000/000/055/129
D204/D307

AUTHORS: Molin, Yu. N., Chhkeidze, I. I., Buben, N. Ya. and Voe-
Vodskiy, V. V.

TITLE: A study of the transfer of energy to aromatic groups during the radiolysis of some organic compounds, by the EPR method


SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962, 326-330






TEXT: The present work is a continuation of an earlier study in which the energy transfers in compounds of type A - D (where A is an aromatic and D an irradiation-unstable substituent) were investigated, D and A behaving respectively as donors and acceptors of energy, to allow a quantitative assessment of such energy transfers. The JEP-2 (EPR-2) apparatus was used, under a beam of 1.6 Mev electrons, the rate of irradiation being 0.03 - 0.3 Mrads/sec. The production of radicals (at 90 - 160°K) increased linearly with increasing doses of irradiation, up to a concentration of $\sim 10^{20}$ per g.
Card 1/3

S/844/62/000/000/055/129
D204/D307

A study of the transfer ...

The radiation yields of radicals, G , were similar in saturated hydrocarbons, as well as in those containing multiple bonds, and were of the order of a few per 100 ev of absorbed energy; they were lower (by a factor of $10^1 - 10^2$) in unsubstituted aromatics than in saturated hydrocarbons and, in aromatic compounds, decreased up to a point with increasing degree of conjugation. In (A-D)-type com-

pounds (I) -R, where R = Me, Et, cyclohexyl, G_{AD} was 0.1 - 1, showing that at $D \rightarrow A$ transfer of energy took place with a probability (α) of 65 - 95%. Energy transfers in (I) and in compounds

(II) -(CH₂)_nSiR₃ (where n = 0, 1, 2, 3 for R = Me and 0.3 for R = Et) led in most cases to the predominance, in the EPR spectra, of lines corresponding to a primary C-H fission in the benzene ring. In compounds (III) --R and R---R',

the EPR spectra were more complex and, with long-chain substituents, lines corresponding to bond fission in the latter began to predominate.
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A study of the transfer ...

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D204/D307

minate. The results are discussed, showing that $D \rightarrow A$ energy transfers occur in all 3 classes of compounds, with high values of α . The assistance of G. K. Voronova and of Ye. D. Kaplan, Ye. A. Chernyshev and V. F. Mironova, members of the Institut organicheskoy khimii AN SSSR (Institute of Organic Chemistry, AS USSR), is acknowledged. There are 2 figures and 2 tables.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics, AS USSR); Institut khimicheskoy kinetiki i gorennya SO AN SSSR (Institute of Chemical Kinetics and Combustion, Siberian Branch of the AS USSR)

Card 3/3

5.3300

11.15.10

43236
S/844/62/000/000/056/129
D204/D307

AUTHORS: Yermolayev, V. K., Molin, Yu. N. and Buben, N. Ya.

TITLE: Recombination of radicals in some frozen organic compounds

SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962, 331-334

TEXT: The present work was aimed at a study of the molecular motions occurring during the recombination of radicals formed under the action of fast electrons at a temperature T_0 , such that n_0 , the number of radicals formed, remains fairly constant over 10 - 15 min. The compounds were then warmed up to a series of temperatures T_i (where $T_i > T_0$), maintained at T_i for 2 min and cooled back to T_0 , at which temperature the remaining concentrations of radicals, n_i , were measured. In crystalline compounds, such as MeOH, C_6H_6 or n-octanol, the radicals disappeared at 0.9 - 1.0 T_m (where T_m =

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Recombination of radicals...

S/844/62/000/000/056/129
D204/D307

m.p.), whilst in poorly crystallizing substances, such as glycerol or *n*-butanol, the recombination took place in the region of vitrification ($0.6 - 0.7 T_m$). This rule was confirmed on slowly frozen (crystalline) and quenched (amorphous) 1,1-dicyclohexyldodecane; cooling at an intermediate rate gave rise to (n_i/n_o) versus $(\frac{T}{T_m})$

plots of an intermediate character, showing the presence of crystallites of varying temperature stability. Such intermediate type curves were the only ones observed for paraffin, polyethylene and polypropylene. The recombination is connected with partial destruction of the lattice and amorphous compounds respectively. In cyclopentane and cyclohexane, in which molecular rotation begins at T_{rot} ($T_{rot} \ll T_m$), it was found that recombination of the radicals took place at T_{rot} , showing that the radicals are probably formed in pairs and recombine as soon as rotation becomes possible. The assistance of V. V. Voyevodskiy and G. K. Voronova is acknowledged. There are 4 figures.

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Recombination of radicals ...

S/844/62/000/000/056/129
D204/D307

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics, AS USSR); Institut khimicheskoy kinetiki i goreniya SO AN SSSR (Institute of Chemical Kinetics and Combustion, Siberian Branch of the AS USSR)

Card 3/3

35062

S/195/62/003/001/003/010

EO71/E136

11.15/10
AUTHORS: Yermolayev, V.K., Molin, Yu.N., and Buben, N.Ya.
TITLE: Recombination of radicals in solid organic substances.
I. Investigation by the method of fusion

PERIODICAL: Kinetika i kataliz, v.3, no.1, 1962, 58-64

TEXT: The range of temperatures at which recombination of radicals takes place on fusion of various organic substances, irradiated with fast electrons, was studied by the β NP (EPR) method. The object of this work was to determine the molecular movements leading to the recombination of radicals in a solid. For this reason the substances investigated had a known phase behaviour on heating. Normal alcohols, ketones, hydrocarbons, aromatic compounds etc. were investigated. To determine the stability of radicals at various temperatures, fusion curves were obtained. For this purpose a substance was irradiated at a sufficiently low temperature T_0 in a stream of fast electrons to obtain a concentration n_0 of radicals. The irradiation was stopped at the beginning of the linear part of the curve of accumulation of radicals ($n_0 \approx 10^{19}$ radicals/g).

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X

Recombination of radicals in solid ... S/195/62/003/001/003/010
EO71/E136

The temperature T_0 was so chosen that during 10-15 minutes no noticeable decrease in the concentration of radicals occurred. The substance was then heated for 2 minutes at a temperature $T_1 > T_0$, cooled to T_0 and the concentration of radicals n_1 measured etc. The dependence $n_i(T_i)$ was called the fusion curve. It was established that for crystalline substances (substances of type I) a rapid recombination of radicals occurs, as a rule, before melting; for amorphous substances the process takes place near the divitrification temperature. For cyclopentane and cyclohexene (type II), radicals recombine near the temperature of their polymorphic transformation. For hexamethylbenzene, acetone, succinic acid (type III) several ranges of recombination of radicals can be separated. In the majority of cases the recombination of radicals is, apparently, caused by self diffusion, appearing close to the temperature of a phase change. For substances of type III the recombination of radicals takes place at a temperature at which the self diffusion of molecules is apparently absent, e.g. in hexamethylbenzene and acetone, radicals recombine partially in the region at which

Card 2/3

Recombination of radicals in solid ... S/195/62/003/001/003/010
E071/E136

the molecules begin to rotate. The recombination of radicals in the absence of self diffusion could be explained by the formation of radicals close to each other, e.g. on the neighbouring molecules in pairs. Then initiation of any molecular movement may lead to their recombination. However, the formation of radicals on neighbouring molecules should be accompanied by a strong widening of components of the superfine structure of the EPR spectra, much higher than was actually observed. The authors thank V.V. Voyevodskiy and G.K. Voronova for their assistance. Part of the material of the present paper was presented at the Second All-Union Conference on Radiation Chemistry. There are 5 figures.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR
(Institute of Chemical Physics, AS USSR)
Institut khimicheskoy kinetiki i goreniya SO AN SSSR
(Institute of Chemical Kinetics and Combustion
SO AS USSR)

Card 3/3

SUBMITTED: August 14, 1961

X

11.9200
11.0132 (also 4223)

42168
S/195/62/003/005/002/007
E075/E436

AUTHORS: Molin, Yu.N., Chkheidze, I.I., Kaplan, Ye.P.,
Buben, N.Ya., Voevodskiy, V.V.

TITLE: Formation of radicals during radiolysis of solid
organic materials. Part I. Comparison of radical
yields in various organic compounds

PERIODICAL: Kinetika i kataliz, v.3, no.5, 1962, 674-679

TEXT: The work was carried out to establish a connection
between molecular structure and probability of its dissociation
into radicals under the action of high energy radiation.
A series of naphthenic and hydroaromatic hydrocarbons with
non-conjugated unsaturated bonds were investigated as well as
some aromatic compounds (di- and triphenyls and phenyl ethers).
The purity of the compounds was 95 to 99%. The solids were
irradiated with fast electrons, the dosage varying between 0.02
and 1 Mrads/sec. Maximum dosage reached 30 Mrads. The yields
of free radicals were determined by electron paramagnetic
resonance at -170 to -110°C using the initial linear part of the
curves relating the numbers of radicals formed to time of
Card 1/3

Formation of radicals ... ; ;

S/195/62/003/005/002/007
E075/E436

irradiation. It was found that for naphthenic and hydroaromatic hydrocarbons the yields amounted to several radicals per 100 eV of absorbed energy. A large yield was also obtained for n-hexadecene-1. Thus the unsaturated bonds in these compounds do not inhibit the radical formation. This conclusion does not agree with that obtained by A. Charlesby and M.G. Ormerod (V. Intern. Symp. on Free Radicals, Uppsala, 1961, paper 11). For the aromatic compounds the yields are smaller by 1 to 2 orders of magnitude. The yields decrease with the increasing number of conjugated double bonds in aromatic molecules and with the increasing degree of substitution of benzene rings with groups containing unshared electron pairs or multiple bonds conjugated with the aromatic system of the molecule. It is concluded that the yield of radicals G_R decreases with the decreasing first excitation energy level E_1 . Especially marked changes in the yield are observed when $E_1 \approx DCH$, where DCH is the energy of rupture of a C-H bond. There are 1 figure and 2 tables.

ASSOCIATIONS: Institut khimicheskoy fiziki AN SSSR
(Institute of Chemical Physics AS USSR)

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Formation of radicals ...

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E075/E436

Institut khimicheskoy kinetiki i goreniya
SO AN SSSR (Institute of Chemical Kinetics and
Combustion SO AS USSR)
Institut organicheskoy khimii AN SSSR
(Institute of Organic Chemistry AS USSR)

SUBMITTED: May 9, 1962

Card 3/3

ZHIDOMIROV, G.M.; MOLIN, Yu.N.

Differences in the widening of separate components of the hyperfine structure in electron paramagnetic resonance spectra of radicals with several α -protons. Zhur.strukt.khim. 3 no.6: 669-675 '62. (MIRA 15:12)

1. Institut khimicheskoy kinetiki i goreniya Sibirskogo otdeleniya AN SSSR, Novosibirsk.
(Radicals (Chemistry)—Spectra)

37433

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B110/B144

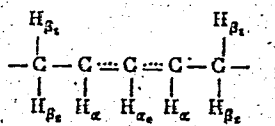
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TITLE: Temperature changes in the epr spectra of allyl and other radicals in irradiated polymers

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 5, 1962, 690-695

TEXT: Oriented samples obtained by fourfold stretching of isotropic polyethylene were irradiated with fast electrons (1.6 Mev, 200 Mrad) and kept at 80°C in an N₂ stream until complete recombination of alkyl radicals was reached. The basic structure of the epr spectra of the allyl radical



of irradiated isotropic low-pressure polyethylene is explained by

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interaction of the unpaired electron with β -protons, and the temperature change of the spectrum is explained by a change of the interaction constant. The five separate components of the spectrum at high temperature correspond to the interaction of the unpaired electron with four β -protons. At low temperature, the β_1 - and β_2 -protons of spectra with seven components are not equivalent, and $\Delta H_{\beta_2} = 2\Delta H_{\beta_1}$. A reversible change of the spectrum with temperature was found. β -protons are equivalent at 80°C, and at 35°C $\Delta H_{\beta_2} = 2\Delta H_{\beta_1}$. The components of the two spectra show doublet separation owing to interaction with the α_0 -proton. For isotropic polyethylene at 95 and -90°C and for oriented polyethylene at 80 and -110°C the authors obtained $\Delta H_{\beta_1} = 19; 13; 18.5; 13.5; \Delta H_{\beta_2} = 19; 26; 18.5; 27; \Delta H_{\alpha} = -; -; 20.5; 19; \Delta H_{\alpha_0} = -; -; 5.5; 5.5$, respectively. The different values of β -hydrogen at low temperatures are caused by a distorted geometrical structure of the radical, which is due to the influence of the crystal lattice of the polymer. Tensions thus occur in the allyl radical at low temperatures.

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They may distort the valency angles and disturb the sp^3 hybridization of the bonds in carbon atoms carrying β -hydrogen atoms. This may lead to an unsymmetrical arrangement of these hydrogen atoms with respect to the plane of the C-C bonds. A temperature rise reduces the influence of the crystal lattice. A four-component spectrum (~ 25 oersteds; 1 : 3 : 3 : 1)

of the radical $\begin{array}{c} H_\beta \quad H \\ | \quad | \\ -C-C-C-N- \\ | \quad | \quad || \\ H_\alpha \quad H_\alpha O \end{array}$ was observed at $36^\circ C$. The unpaired electron

reacts with one α - and two β -protons. As with the allyl radical, a drop in temperature changes the number of components. There are 4 figures and 1 table.

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